

Structural Dynamics in Metallic Glasses Using High Energy X-rays

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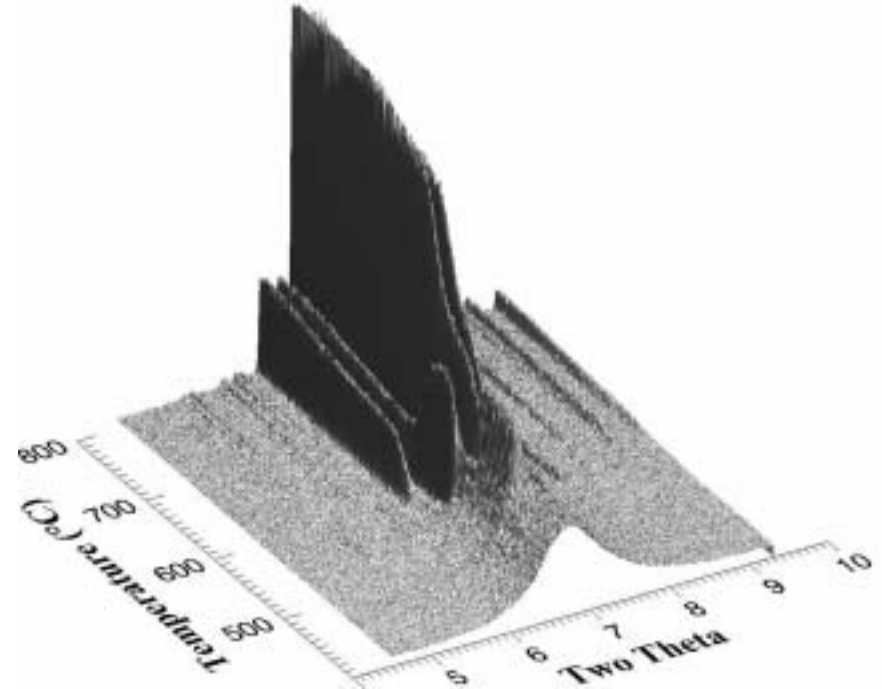
APS High Energy Workshop

9-10 August, 2004

Prospects for In-Situ HEXRD



- **Kinetic Studies of Phase Transformations in Bulk**
 - Solid – Solid
 - Solid – Liquid
 - Magnetic
 - ↓ Magnetoelasticity
 - Atomic motions
- **Crystal Chemistry**
 - Interstitial/Vacancy Distribution
 - Coefficients of Thermal Expansion
- **Disorder Systems?**



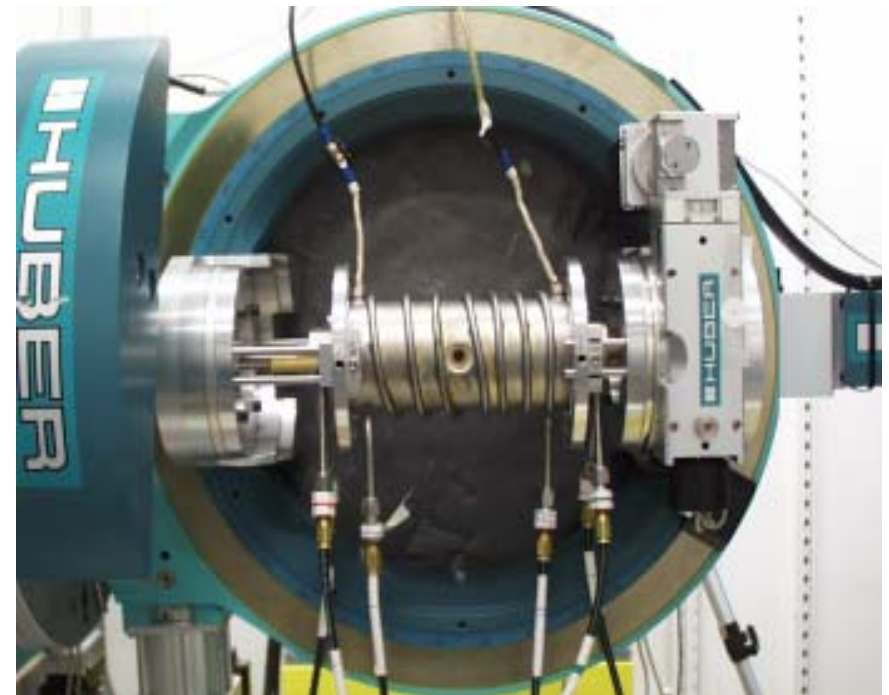
Example of *in situ* devitrification of a Ti-Zr-Cu-Ni amorphous alloy

Requirements



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- **Fast data acquisition**
- **Good S:N**
- **Furnace Design**
 - **Eulerian Cradle**
 - **Very low lateral and radial thermal gradient ($\sim \pm 2^\circ\text{C}$ over 4 mm distance)**
 - **$\sim 1800\text{ K}$**
 - **Inert to Oxidizing**
 - **Sample rotation for improved powder averaging**
 - **Sample Containment**
 - **Uniform Heating**



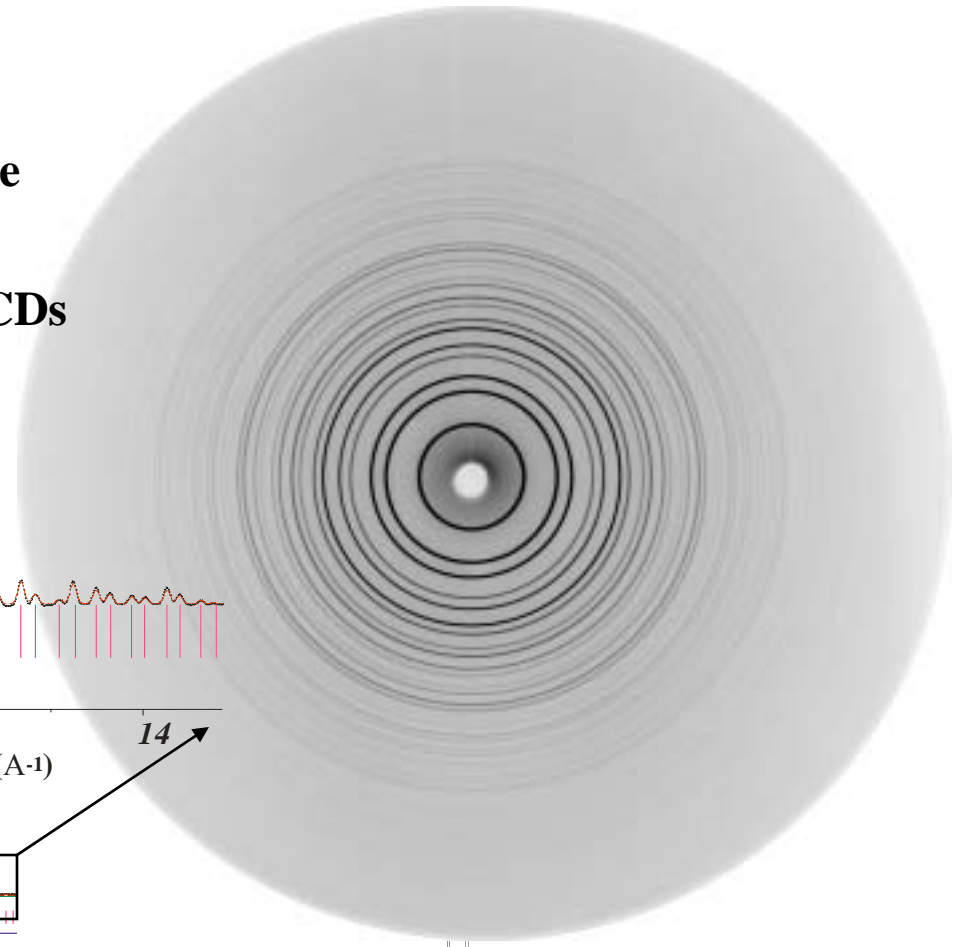
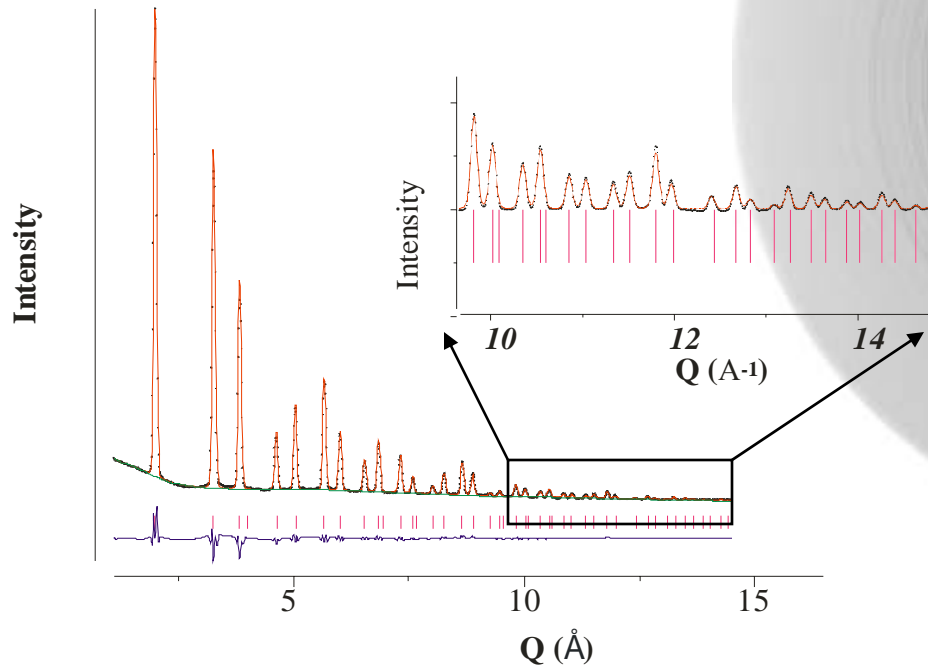
Data Acquisition



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➤ MAR3450

- ↓ Fixed Position
- ↓ Single Frame per exposure
- ↓ Longer cycle time
- ↓ Larger area than most CCDs



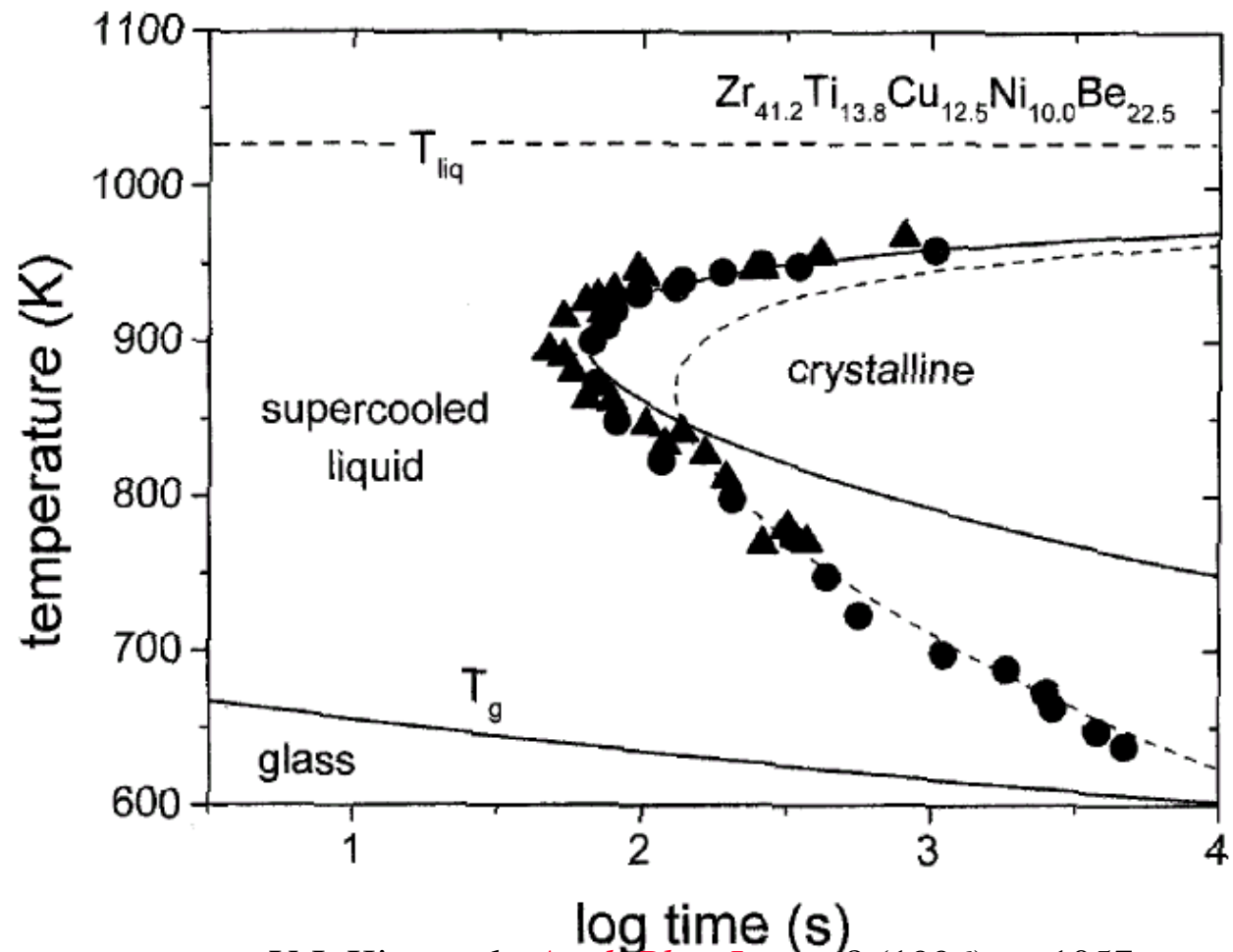
0.1065 \AA , $d_o = 0.635 \text{ m}$

Data Acquisition



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- For Amorphous Structural Dynamics
 - Relaxation rate
 - Nucleation rate
- For Solid-State Phase Transformations
 - Displacive
 - Reconstructive
- For Liquid-Solid Transformations
 - Degree of undercooling



Y.J. Kim et al., *Appl. Phys. Lett.*, 68 (1996), p. 1057.

Amorphous or Liquid 'disordered' State



Reciprocal Space Measurement

- Measured intensity $I(Q)$
- Corrected for background and Compton Scattering
- Difference in the local atomic number density from the average density
 - ↓ a_i is the concentration
 - ↓ f_i is the scattering factor

Real Space Determination

- Fourier transformation of $S(Q)$

$$S(Q) = 1 + \frac{\left[I^e(Q) - \sum_{i=1}^n a_i |f_i(Q)|^2 \right]}{\left| \sum_{i=1}^n a_i f_i(Q) \right|^2}$$

Reduced Distribution Function

$$G(r) = \frac{2}{\pi} \int_0^{Q_{\max}} Q [S(Q) - 1] \sin(Qr) dQ$$

Atomic Pair Distribution Function

$$g(r) = \frac{G(r)}{4\pi r \rho_0} + 1$$

where $Q = \frac{4\pi \sin(\theta)}{\lambda}$

But there is more information!

- With high S:N, what does the difference in the total scattering function, $S(Q)$, from one time step to the next show?

- If the structure is changing, the $\Delta S(Q)$ should show not only how, but how much.

$$\Delta S(Q) = S(Q) \Big|_{t+\Delta t} - S(Q) \Big|_t \approx \frac{\frac{I(Q) \Big|_{t+\Delta t}}{\sum_{Q_{\min}}^{Q_{\max}} I(Q) \Big|_{t+\Delta t}} - \frac{I(Q) \Big|_t}{\sum_{Q_{\min}}^{Q_{\max}} I(Q) \Big|_t}}{\frac{\sum_{i=1}^n |a_i f_i(Q)|^2}{\sum_{Q_{\min}}^{Q_{\max}} \sum_{i=1}^n |a_i f_i(Q)|^2}}$$

- The rate of the change should reflect the volumetric change with time

$$F = \sum_{t_o}^{t_f} \frac{dS(Q)}{dt}$$

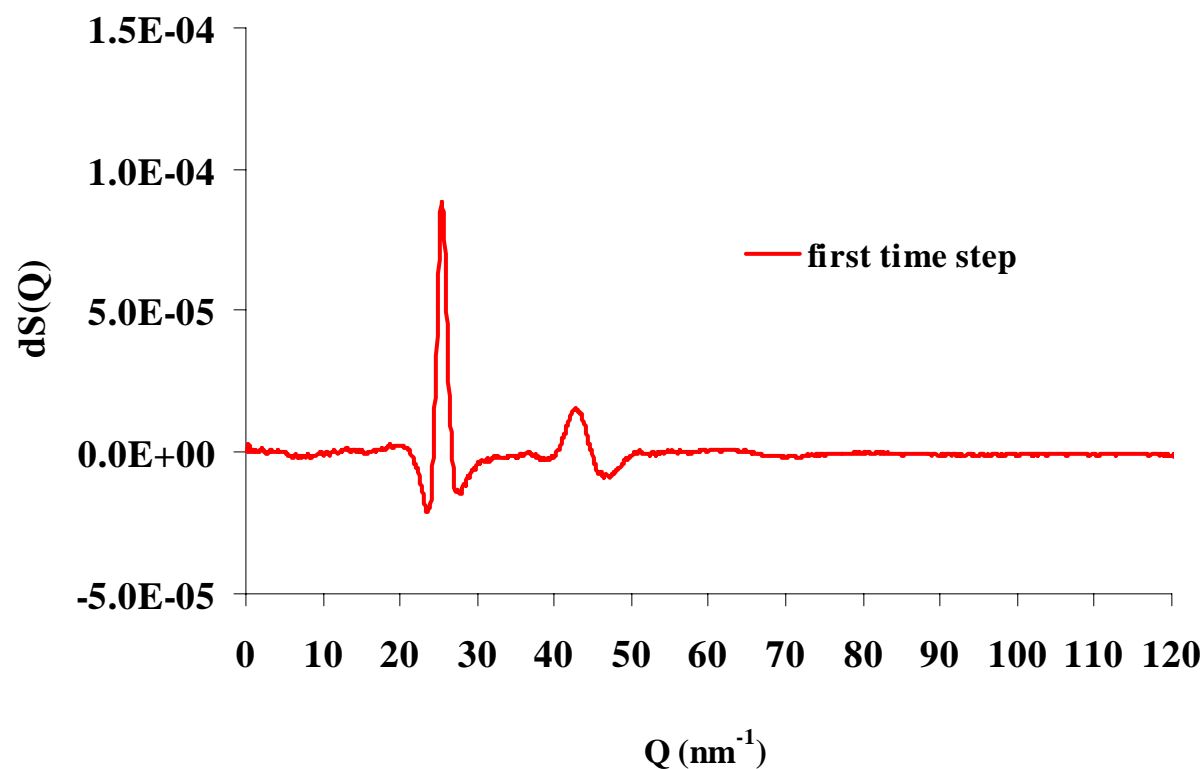
- So we can extract out the diffraction pattern of only the nucleating phases

$$I_f(Q) = I(Q) \Big|_{t_f} - I(Q) \Big|_{t_o} * (1 - F)c$$



What we don't see with a casual observation

- Amorphous $\text{Zr}_{70}\text{Pd}_{20}\text{Cu}_{10}$
- Heated to 630 K
- Compare after 400 s at T



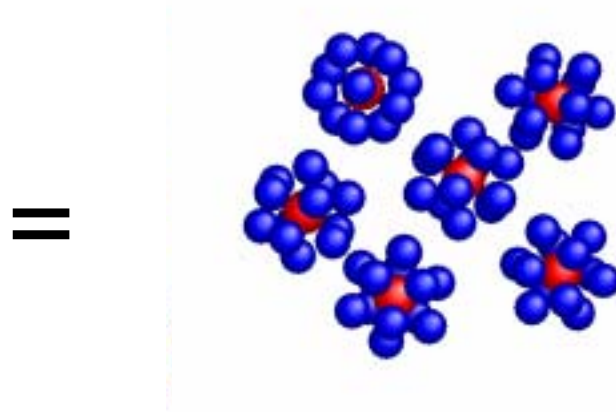
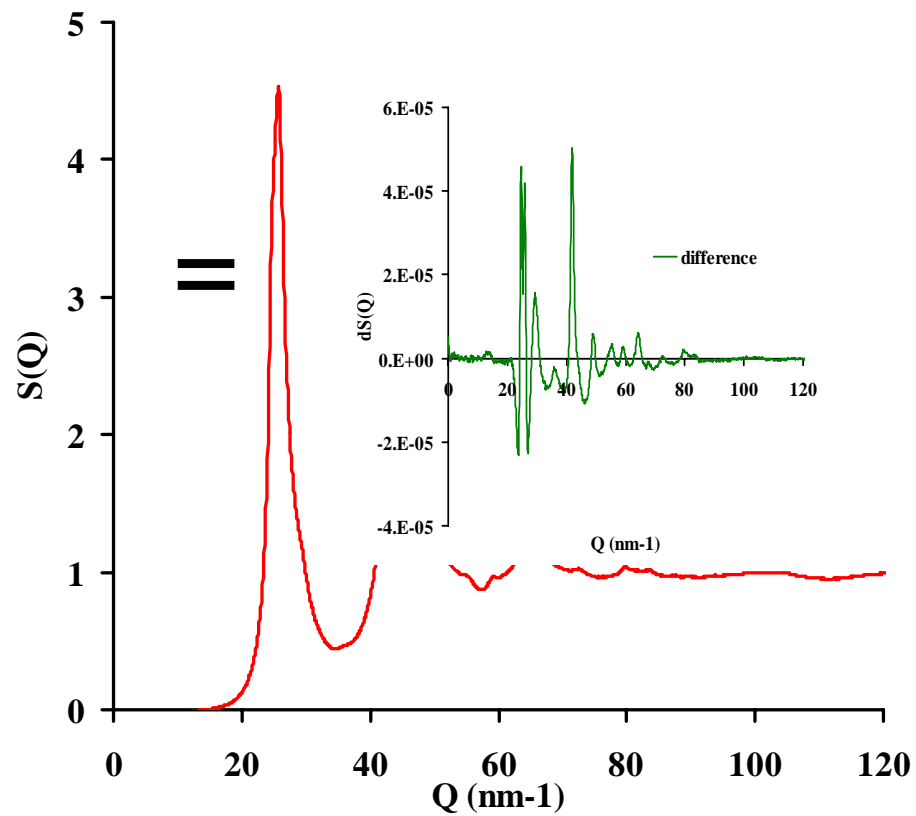
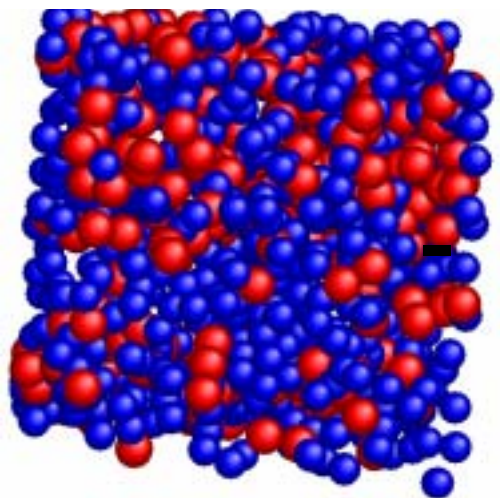
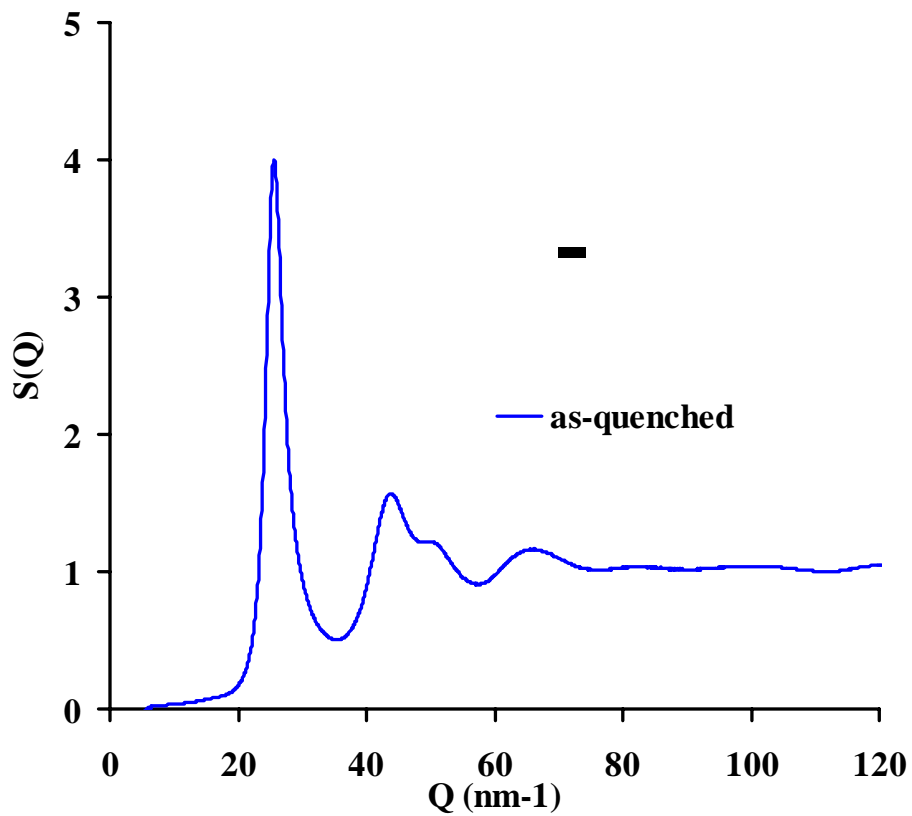
Example, Structural Relaxation and Nucleation of a Metallic Glass

- **Rapidly solidified $\text{Zr}_{70}\text{Pd}_{20}\text{Cu}_{10}$**
- ***In Situ* heat at a $T < T_g$**
- **Compare the changes in $S(Q)$ with time**
 - **Observe the structure of the crystallizing phase**
 - **The rate of the change should reflect the volumetric change with time (i.e, JMA should hold true)**
 - ↓ **The phase fraction transformed and the kinetics between the DSC and the HEXRD should be equivalent!**

$$F = \sum_{t_o}^{t_f} \frac{dS(Q)}{dt} \qquad F = 1 - e^{(kt^n)}$$

Kramer, M. J., M. F. Besser, et al. (2003). "Devitrification studies of Zr-Pd and Zr-Pd-Cu metallic glasses." Journal of Non-Crystalline Solids **317**(1,2): 62-70.

Kramer, M. J., M.F. Besser, E. Rozhkova, and D.J. Sordet, "Influence of Short-Range Order on Devitrification in $\text{Zr}_{70}\text{Pd}_{20}\text{Cu}_{10}$ Metallic Glasses", *Intermetallics*.

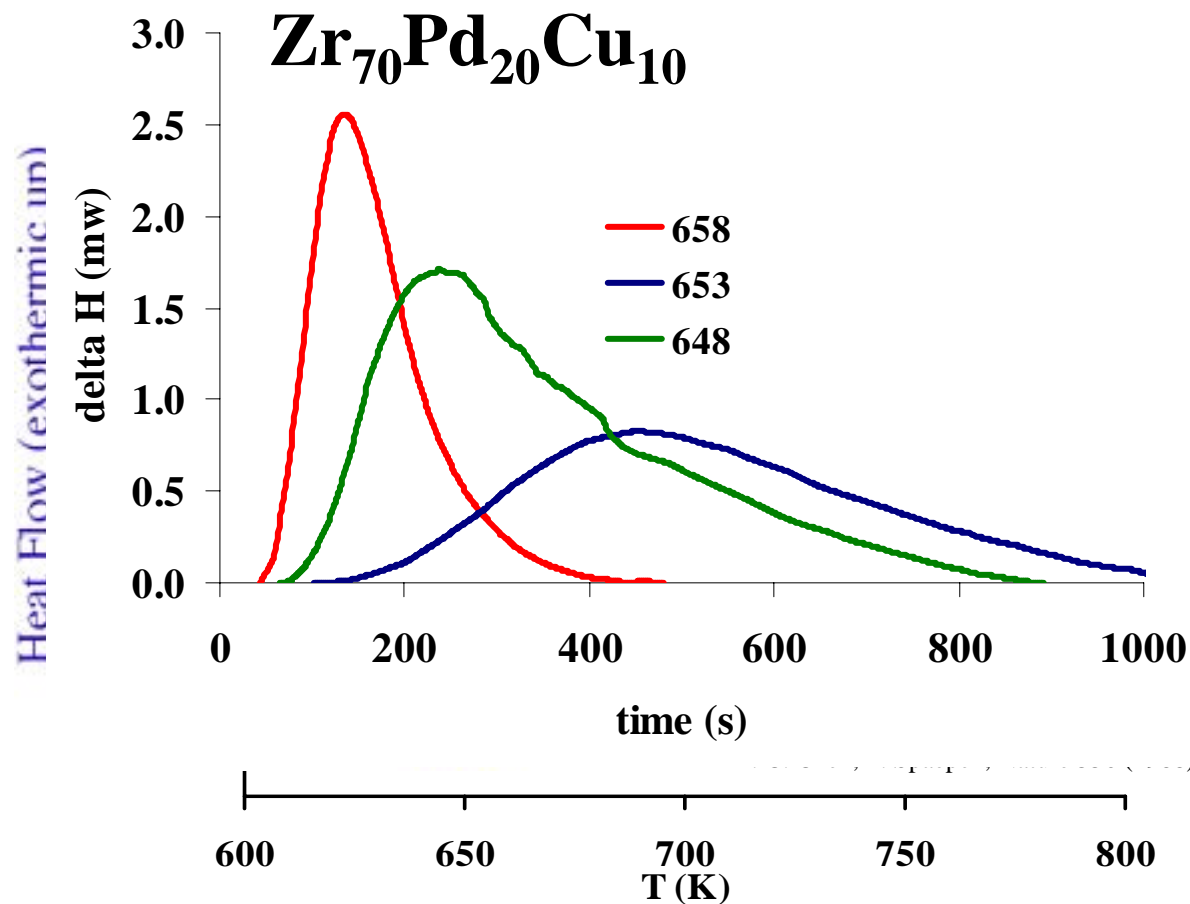


Structural Relaxation



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- Can we follow the structural changes during an isothermal anneal below T_g ?

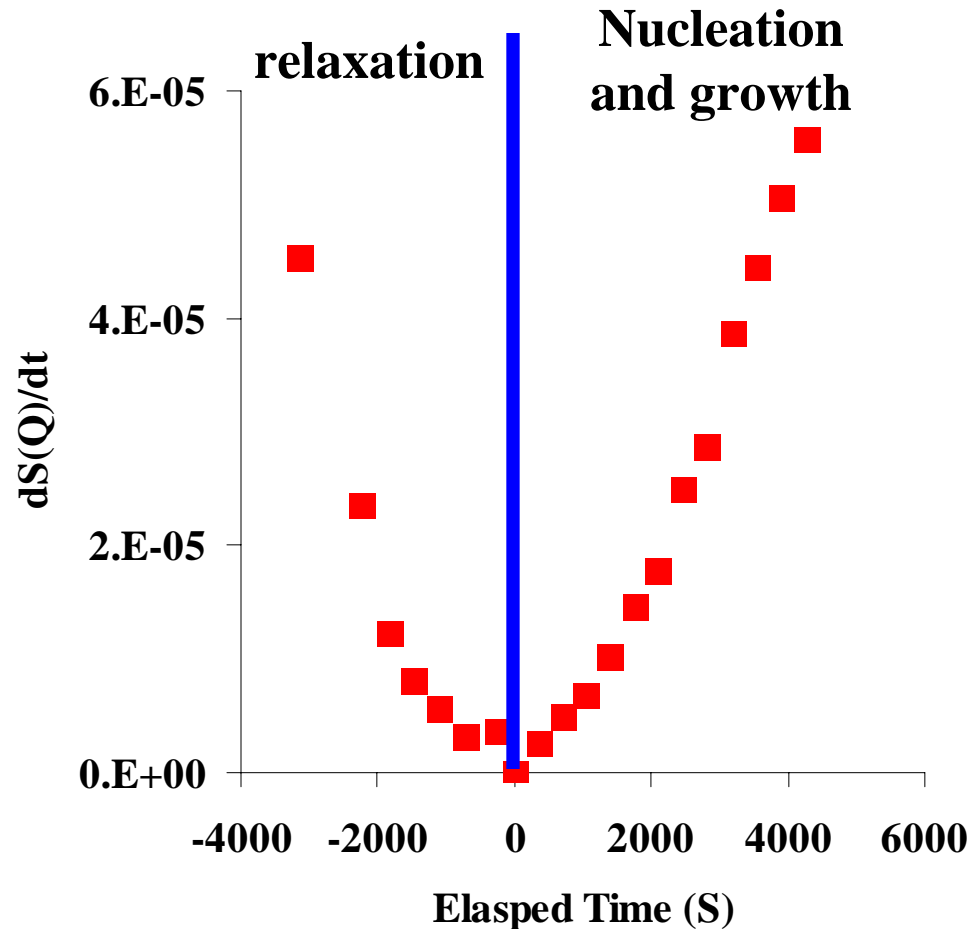


Structural Rate Change



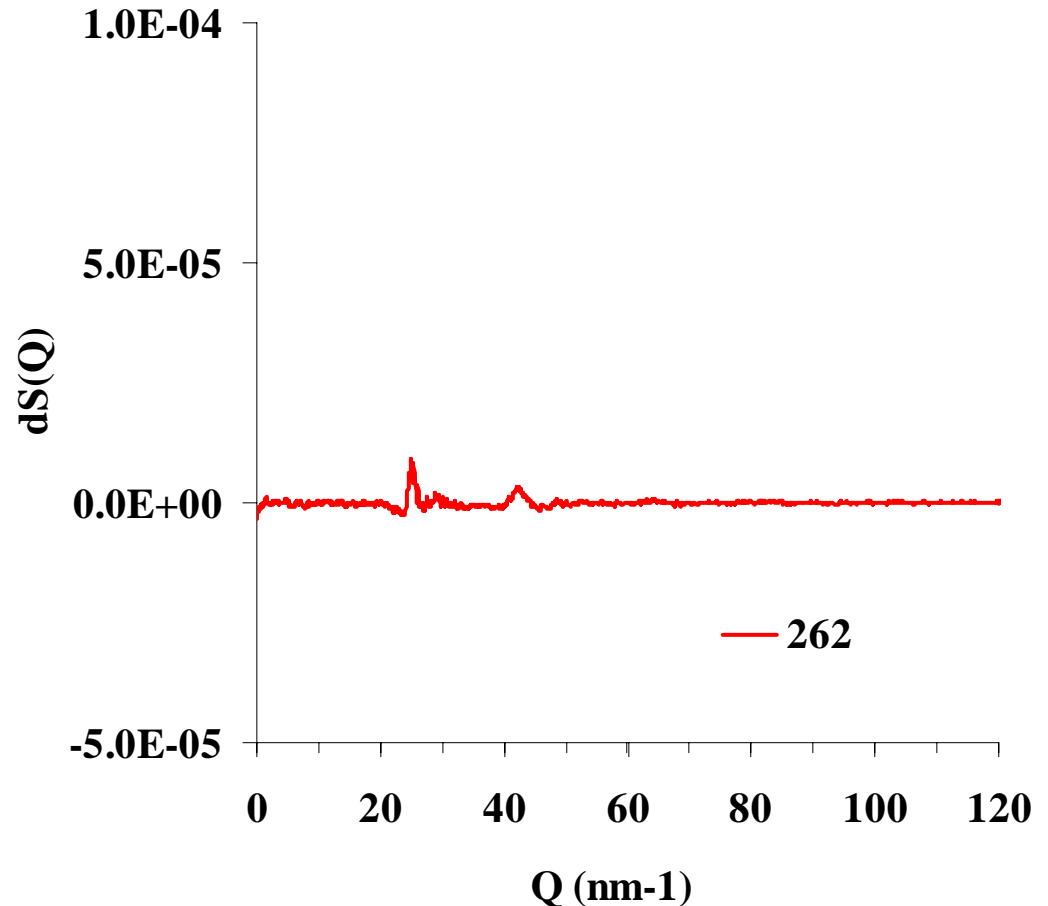
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- $\Delta S(Q)/dt$ should then follow the DSC trend if they are both measuring the same phenomena.
- Set the minima to be the demarcation from relaxations to nucleation and growth



Structural Relaxation, cont.

- If relaxation proceeds nucleation, the rate of change should decrease with time, corresponding to the DSC results.

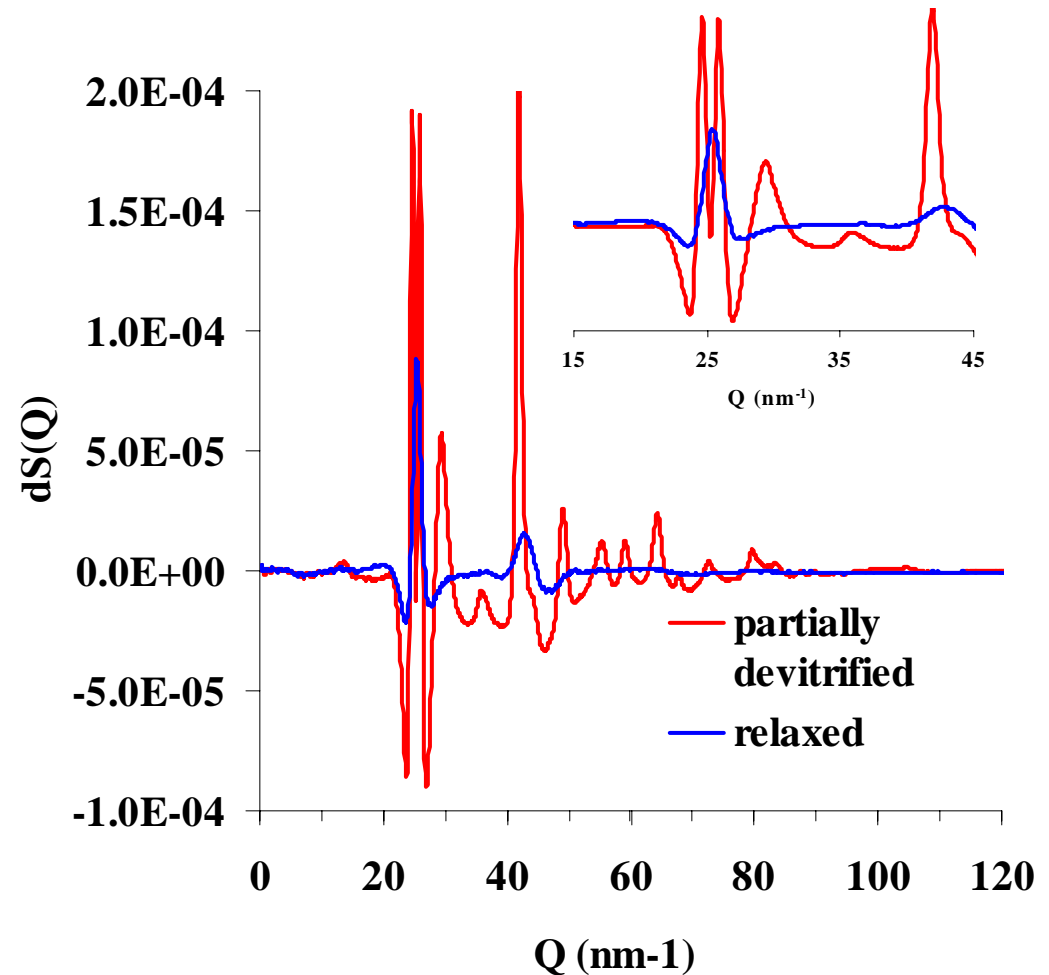


Relaxation vs Devitrification, $\Delta S(Q)$



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- $\Delta S(Q)$ increases w/ time at T
- Clear differences in $\Delta S(Q)$ between the relaxation and nucleation



Johnson-Mehl-Avrami



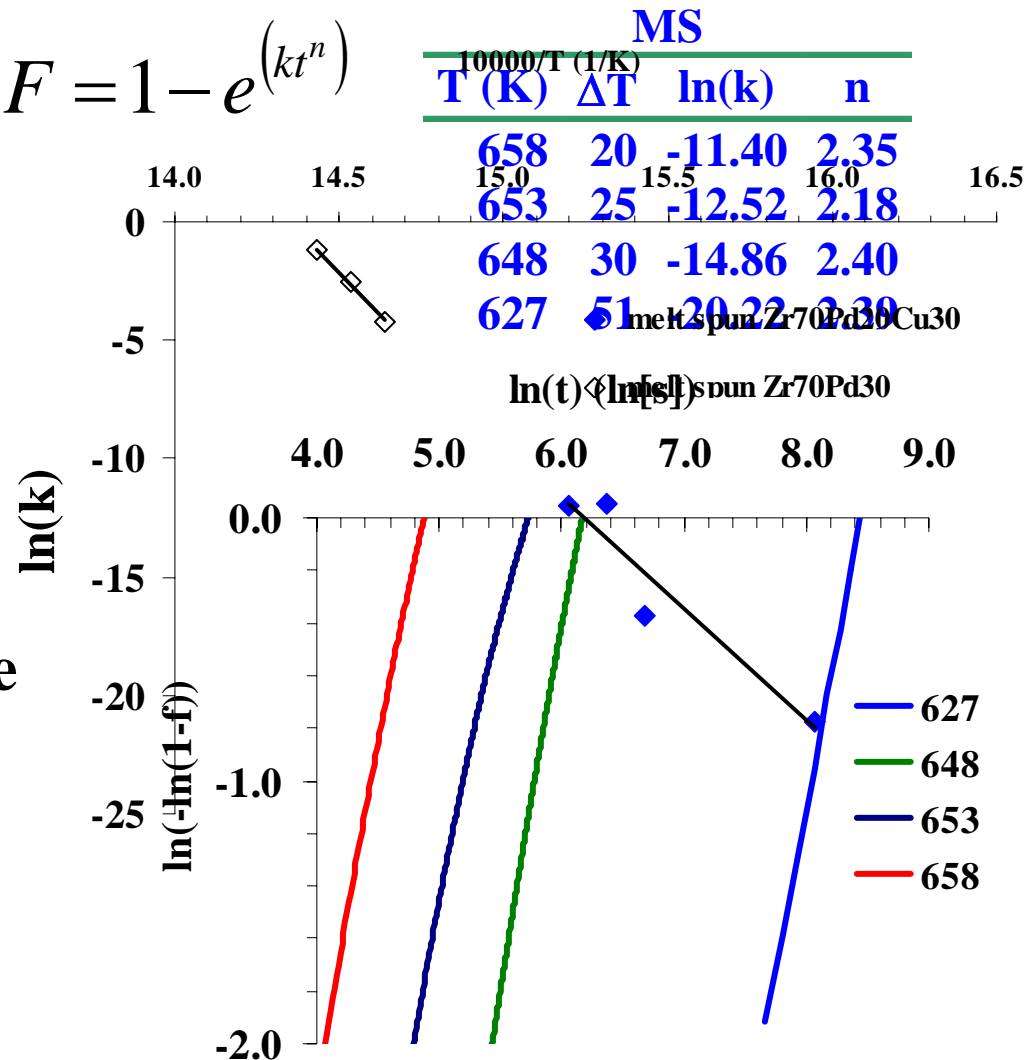
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- Volume Fraction

- ln(k) values DSC and HEXRD data are linear
 - n values are also consistent

- Confirms that the HEXRD and DSC are measuring the same phenomena

$$F = 1 - e^{-(kt^n)}$$

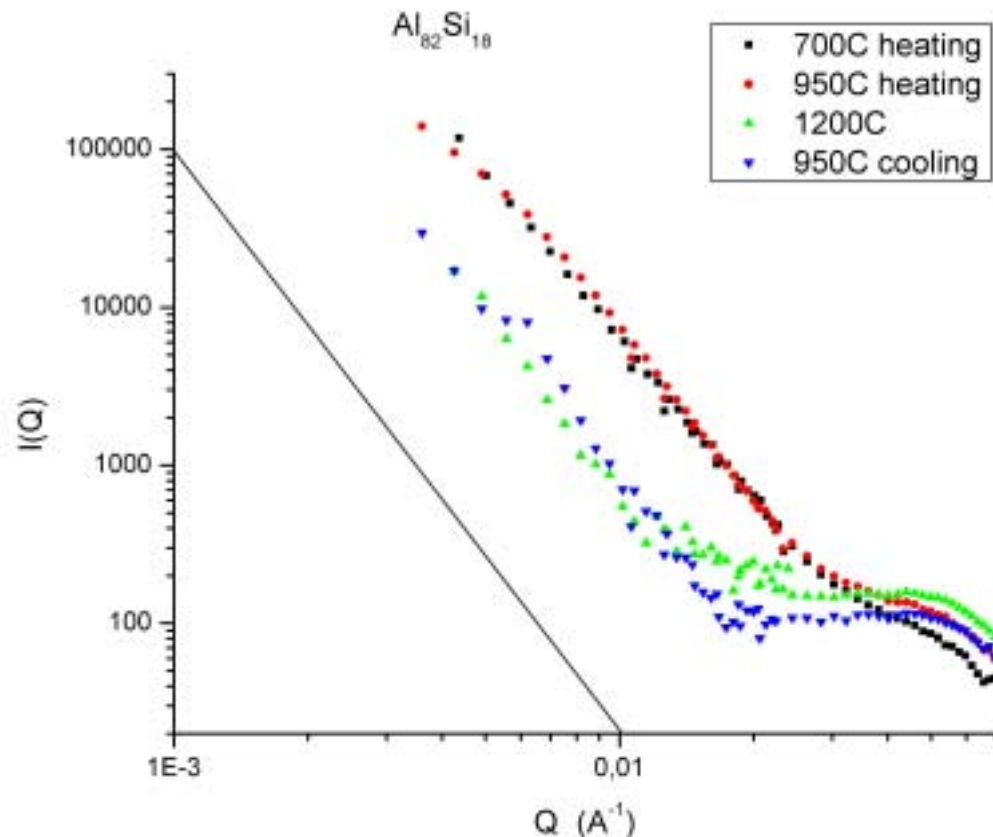


Can we do the same for a liquid system?



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- **Subtler differences**
 - Changes in short-range order (SRO)
 - Pair-Pair correlations only
 - ↓ 3 body correlations may be necessary
- **Evidence for Structural Changes in the Liquid State**
 - 1st or 2nd order
 - Chemistry effects
- **Can diffraction be used to refine simulations?**

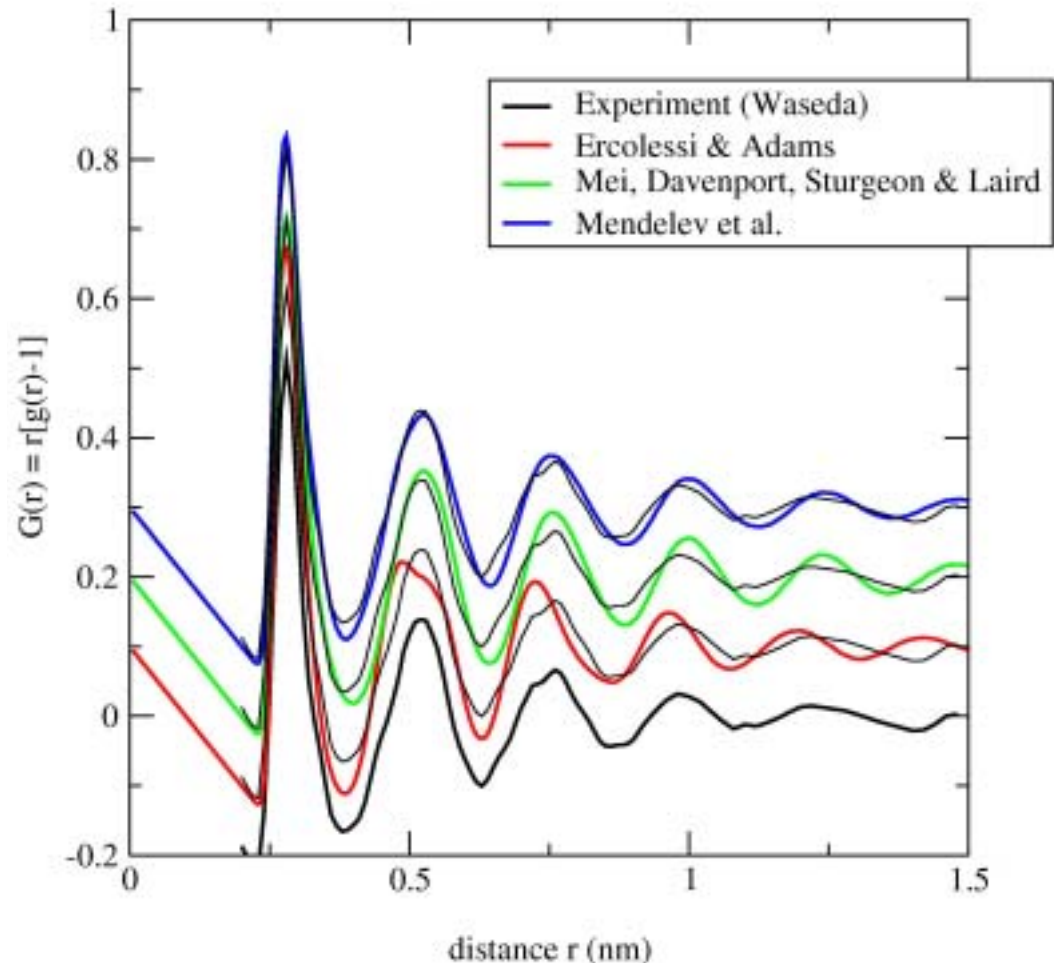


Comparing structure of liquid Al



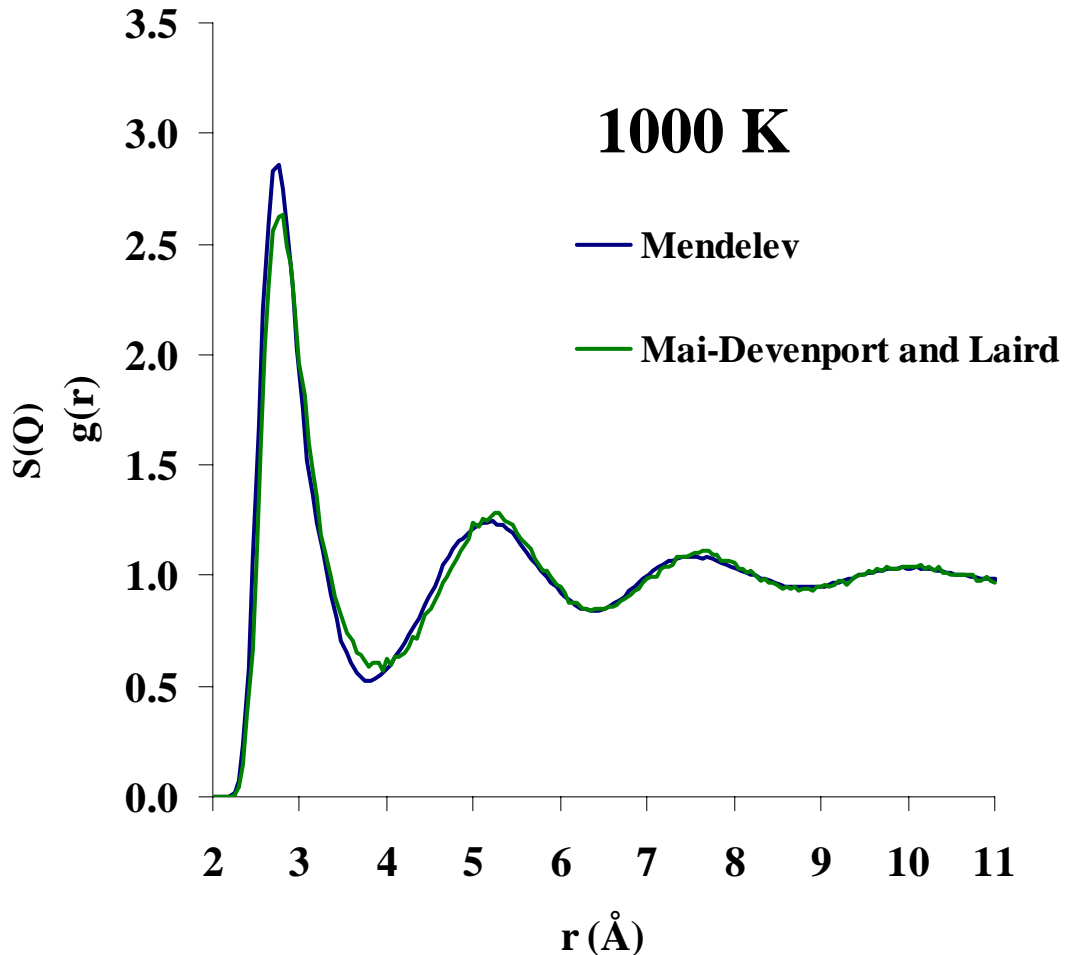
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- Structure of MDL and Mendelev *et al* potentials are close to experimental results. Very close to a “hard-sphere” liquid.
Song and Morris, PRB 2003.
- Ercolessi & Adams potential is more “icosahedral” and has higher interfacial free energy.
- Suggests correlation between structure of liquid and interfacial free energy.



Structure of liquid Al, theory and experiments

- What is the best way to compare, $S(Q)$ or $g(r)$?
- How accurate are the absolute pair-pair correlations?
- Is icosahedral order intrinsic or an artifact of the potentials?



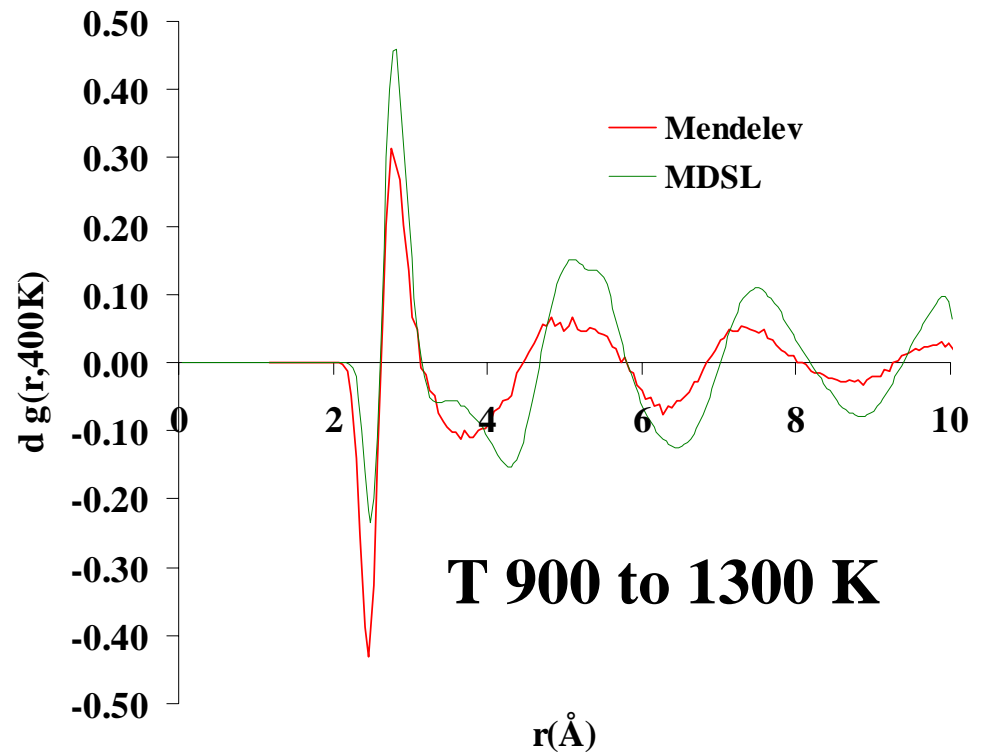
Comparing structure of liquid Al

- Icosahedral structure can be seen more clearly in the *change* in $g(r)$ (or $S(Q)$) with temperature.
- Sequential X-ray or neutron scattering data can then be used to validate the models.

Ercolessi & Adams potential

Mei, Davenport,

Sturgeon & Laird potential



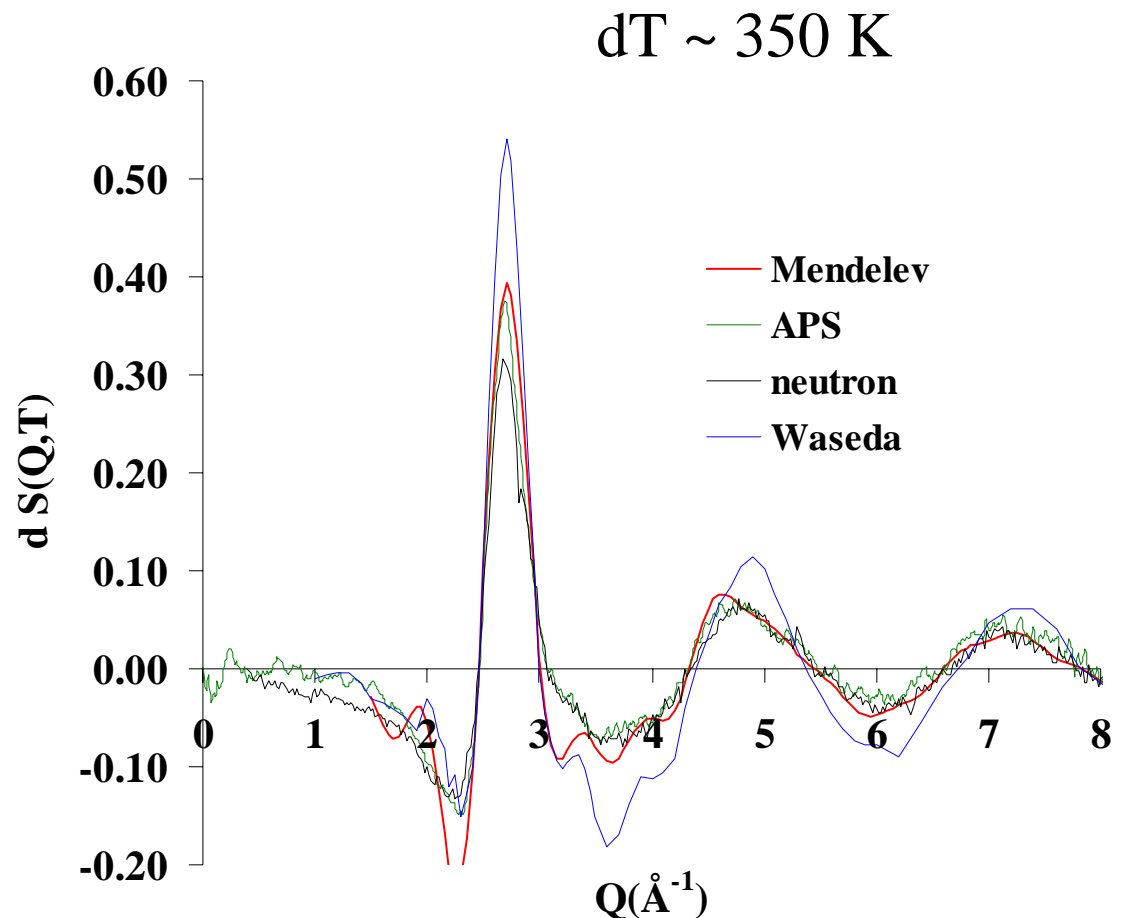
Position of icosahedra peaks
(Leung & Wright, Phil. Mag. 1975)

Experiments vs Models

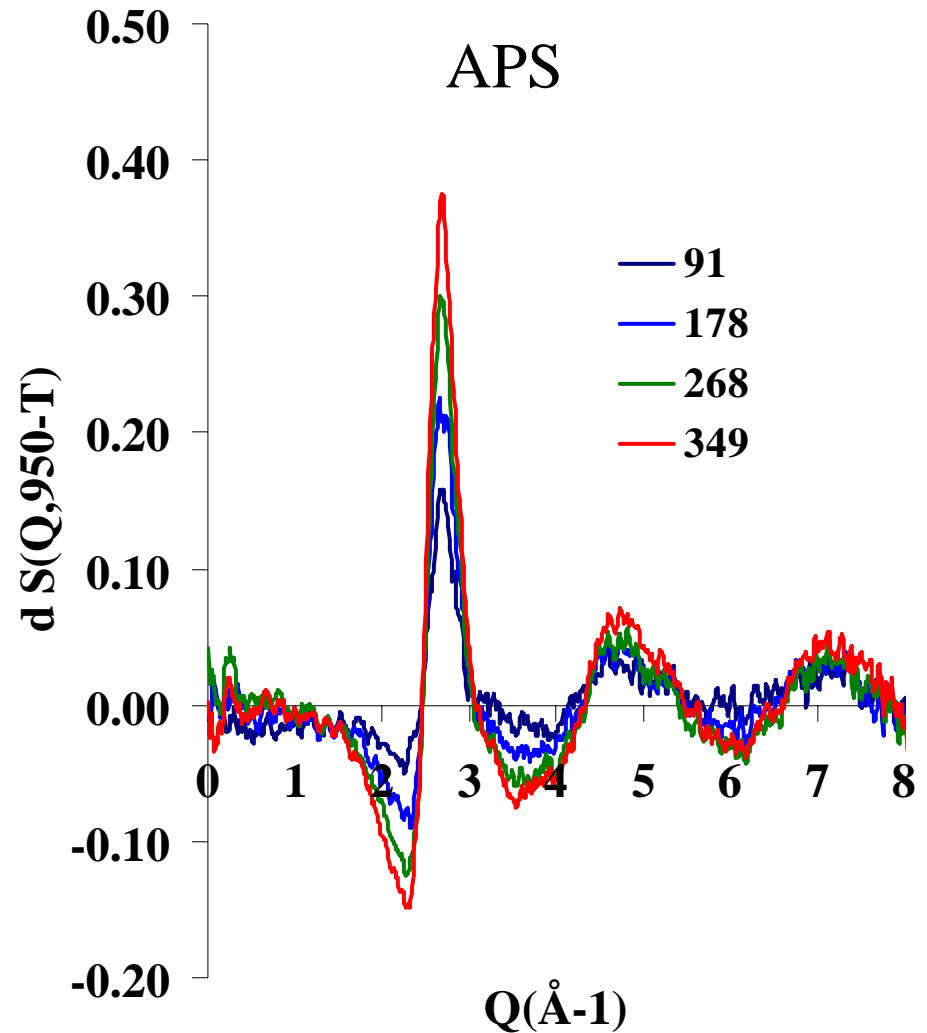
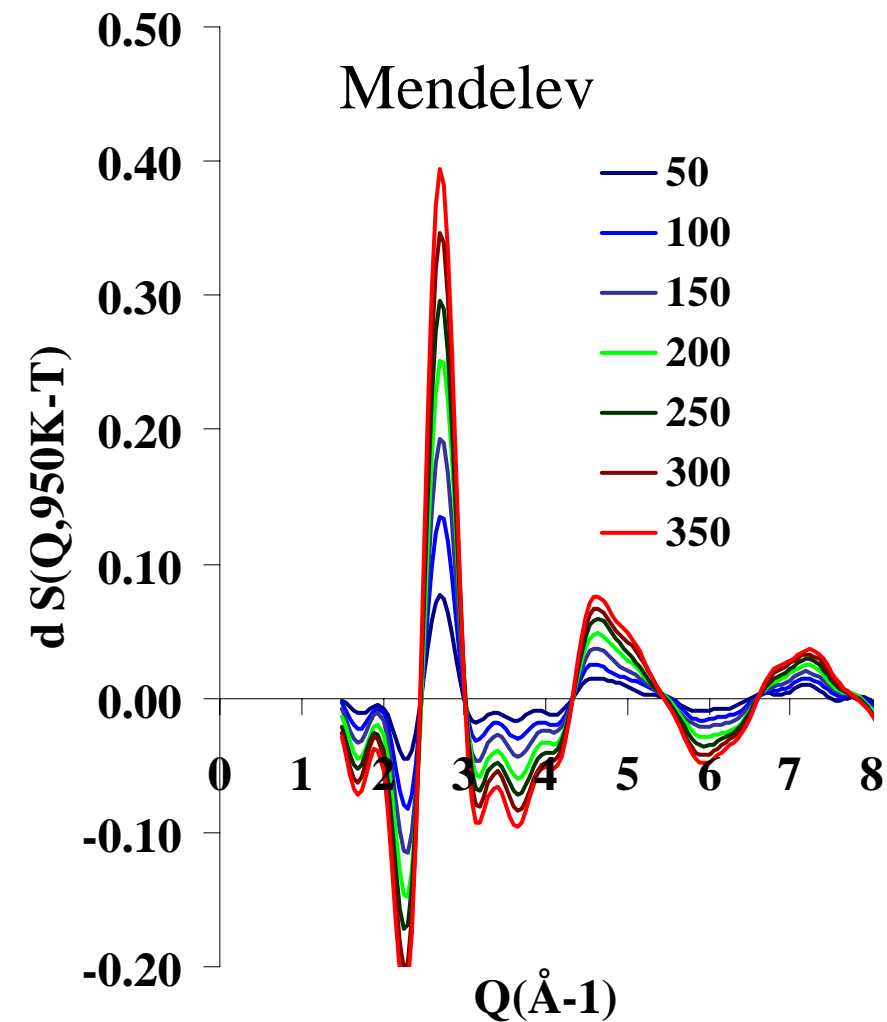


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- Comparing $S(Q)$
 - fewer artifacts from FFT
- HEXRD and neutrons compare very well
 - Artifacts easier to eliminate
 - Apparent icosahedral order disappears

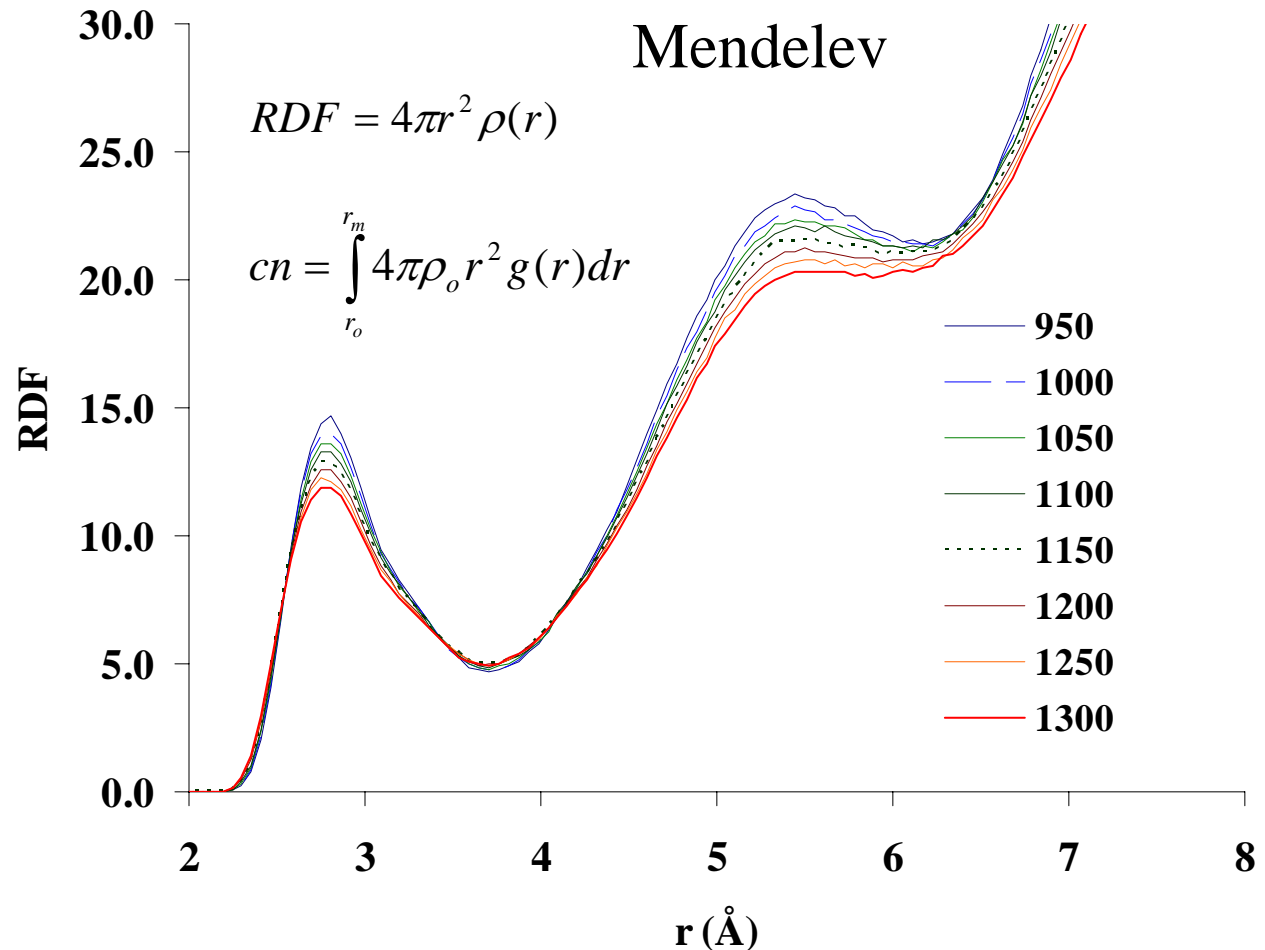


Experiment vs Model



Changes in the Short Range Order?

- E&A and MDSL increase in local order with decreasing temperature, which is consistent with increase in icosahedral order
- Mendelev potential shows a more modest increase in order with no obvious icosahedral order
- **Caution! 3 body correlations need to be performed**



Conclusions

- **HEXRD is a powerful tool to investigate the structure of ‘disordered’ as well as ordered systems**
 - Full samples penetration eliminates many sample artifacts
 - Many containment systems can be brought to bear
 - Rapid data acquisition and high S:N allows for time, temperature sequential data sets to be taken on the second to minutes
 - ↓ But we need to collect data faster without loss of S:N!
- **Rapid sequential sampling is shown to be an excellent method for comparing MD simulations where time and spatial scales are difficult to correlate**
- **We are not ‘flux’ limited’ but detector limited.**
 - However, focusing is crucial with higher data rates
 - Systematic structural studies requires stable optics

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